

X-ray standing wave imaging of atomic layer deposited (ALD) tungsten monolayers on α -TiO₂(110)

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Introduction

Ultra-thin metallic or metal-oxide layers deposited onto oxide surfaces have wide applications in microelectronics, catalysis, photonics and chemical sensing [1-3]. During the past decade atomic layer deposition (ALD) provides outstanding control over the synthesis of supported materials due to its capacity for self-terminating conformal layer formation [4]. For example, ALD has been used for high-k dielectric film growth [5] and for processing catalysts on porous or dispersed high surface area substrates [1]. Despite its successful applications, the ALD method lacks a detailed atomic-scale understanding of the formed interface structure.

The X-ray standing wave (XSW) method has long been used to study a bonding geometry of surface adsorbates [6]. Recently, a model-independent, element-specific direct imaging technique has been developed based on the Fourier synthesis of XSW data [7]. This presentation, which is based on our recent publication,[8] demonstrates how the XSW imaging method was applied to a sub-monolayer W film grown by ALD on a rutile (110) substrate.

Methods and Materials

The tungsten overlayer of 0.38 monolayer was grown on a α -TiO₂(110) substrate. In order to achieve an atomically flat surface (as verified by AFM) the substrate was annealed in air at 950 °C for 4 hours. Hydroxylation of the TiO₂ surface was achieved by UV radiation ($h\nu=240$ nm) exposure, immersing in water at 90 °C, followed by a dilute HCl rinse and then blow-dry with N₂. In the ALD reactor [9] the tungsten film was deposited with sequential exposure of Si₂H₆ and WF₆ at 10 Torr for 10 minutes, respectively. After one cycle of exposure the substrate was taken out of reactor and place on a 4-circle diffractometer for X-ray standing measurements at the 12ID-D Advanced Photon Source station. An incident photon energy of 13.5 keV was selected with Si(111) monochromator and collimated further with either Si(111) or (220) channel cuts. A solid state detector was used to collect fluorescence from the sample. XSW modulation of W L β fluorescences were used to get coherent position and coherent fraction.

Results and Discussion

The XSW measured set of hkl Fourier components for the W atomic distribution function are summed together to produce a model-independent 3D map of the W atoms relative to the rutile lattice. (See Fig. 1.) The XSW results show that tungsten has an average adsorption height of 3.48 Å above Ti-O plane. The 3D atomic image shows surface tungsten atoms equally occupying the two non-equivalent Ti sites with a slight outward displacement. This corresponds to the atop and bridge sites with respect to the underlying lattice oxygen atoms. The least squares fit to the measured f and P values indicates that two symmetrically non-equivalent W sites are occupied with the

same occupation fraction and the bridge site and atop site tungsten atoms locate 0.35 ± 0.08 Å and 0.03 ± 0.08 Å higher than ideal Ti sites, respectively. These XSW measurements clearly show that ALD conformal layers can be highly coherent with respect to the substrate lattice. AFM images from before and after the ALD process also verify the conformal nature of the deposition.

Acknowledgments

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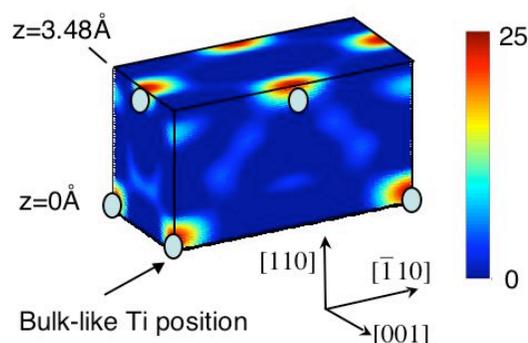


FIGURE 1. Measured distribution of W adsorbed on rutile (110) shown as a cut through the plane of maximum density (scale bar shown at right). Open circles denote Ti sites at height of 0 and 3.25 Å expected in ideal extension of substrate above surface

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